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SOURCE AND AMBIENT SAMPLING RELATING TO THE POWER INDUSTRY IN NORTH AMERICA

by

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ABSTRACT

The following report documents the state of environmental monitoring relating to the combustion of fossil fuels in North America. The basic concepts of manual source sampling for particulates, SO_2, NO_x and in-stack sizing are covered. The principles of operation of continuous emission monitors are discussed. The particulate material once removed from the source becomes a problem for ambient sampling. The proposed new standard (PM-10 regulations) and the sampling strategy for measurement are discussed.

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1 INTRODUCTION

The combustion of coal, oil and natural gas supplies about 95% of the total heat energy used in the United States and Canada. The need to monitor emissions of pollutants from stationary sources arises from federal and provincial/state regulations governing the discharge of pollutants into the atmosphere. The regulations are designed to protect the public health and welfare as well to protect the environment.

Regulations governing the discharge of particulates, sulfur dioxide (SO_2), nitrogen oxides (NO_x) and sulfuric acid mist have been in force for approximately 15 years in North America. More recently regulatory bodies have been concerned with toxic chemical emissions from industrial, residential and transportation sources.

Monitoring of emissions of volatile and semi volatile organic compounds, especially after incineration from toxic waste dumps, has been a high priority of the U.S. Environmental Protection Agency (US EPA), one of the primary regulatory bodies in North America.

2 MANUAL SOURCE SAMPLING

2.1 Particulates

Standardized tests for velocity determination, moisture content, flue gas composition, temperature and static pressure must be determined before sampling for particulates. The objective in sampling for particulates is to extract a portion of the gas stream isokinetically, i.e. to extract a sample through the nozzle at the same velocity as the stack.

The number of traverse points required for particulate sampling depends on the downstream disturbances (bends in the pipe, fans, constrictions, etc.) and the stack diameter. If there are eight stack diameters downstream without obstructions then one does not have to increase the prescribed number of sampling positions, normally two traverses at ninety degrees are required per test.

The stack velocity is determined using a S-type pitot tube, as they are less prone to plugging than the standard types. The S-type pitot tubes must meet proper specifications of alignment along the transverse and longitudinal tube axis. In this way one ensures proper velocity measurements across the stack.

Moisture is condensed from the gas stream by collecting the water vapour at temperatures greater than 100^{o}C (heated probe and filter sections) then condensing the moisture in glass impingers placed in an ice bath. The final impinger contains self-indicating silica gel for complete removal of moisture. The impingers are weighed before and after sampling to determine the mass of water collected. A vacuum pump moves the stack gas through the sampling train while all particulates are

trapped on a heated glass fiber filter paper (Figure 1). Prior to sampling a flue gas analysis is performed using an Orsat apparatus to determine CO_2, O_2 and CO percent by volume. The nitrogen content is calculated by difference.

Prior to the actual particulate test, calculations are made for selection of the appropriate nozzle. In this way proper isokinetic sampling can be achieved. The proper flow through the sampling train is maintained at each sampling position by monitoring the velocity pressure in the stack and adjusting the flow controller valves in relation to the pressure drop across an orifice plate. An inclined manometer records the pressure differences for both the pitot tube and the orifice plate.

After the prescribed number of sampling positions have been completed for each traverse the train is removed for extraction. Normally water and acetone are used for washing out the nozzle, probe, cyclone and impingers. The filter is dessicated and reweighed for determination of particulate mass. The other components of the sampling train are evaported to dryness and the remaining mass is determined. The final results are expressed as a concentration, the units are grams per dry reference cubic metres (g/drm^3) where reference conditions are 101.3 KPa and 25^oC. The results can be expressed on a 3% or 6% O_2 basis, a 12% CO_2 basis or to 50% excess air. The result of correcting the emissions to 6% O_2 or 12% CO_2 allows a degree of standardization when comparing combustion of different types of coal.

Results are sometimes expressed as emission rates in terms of the energy input of the coal, for example, for coal residue fired boilers

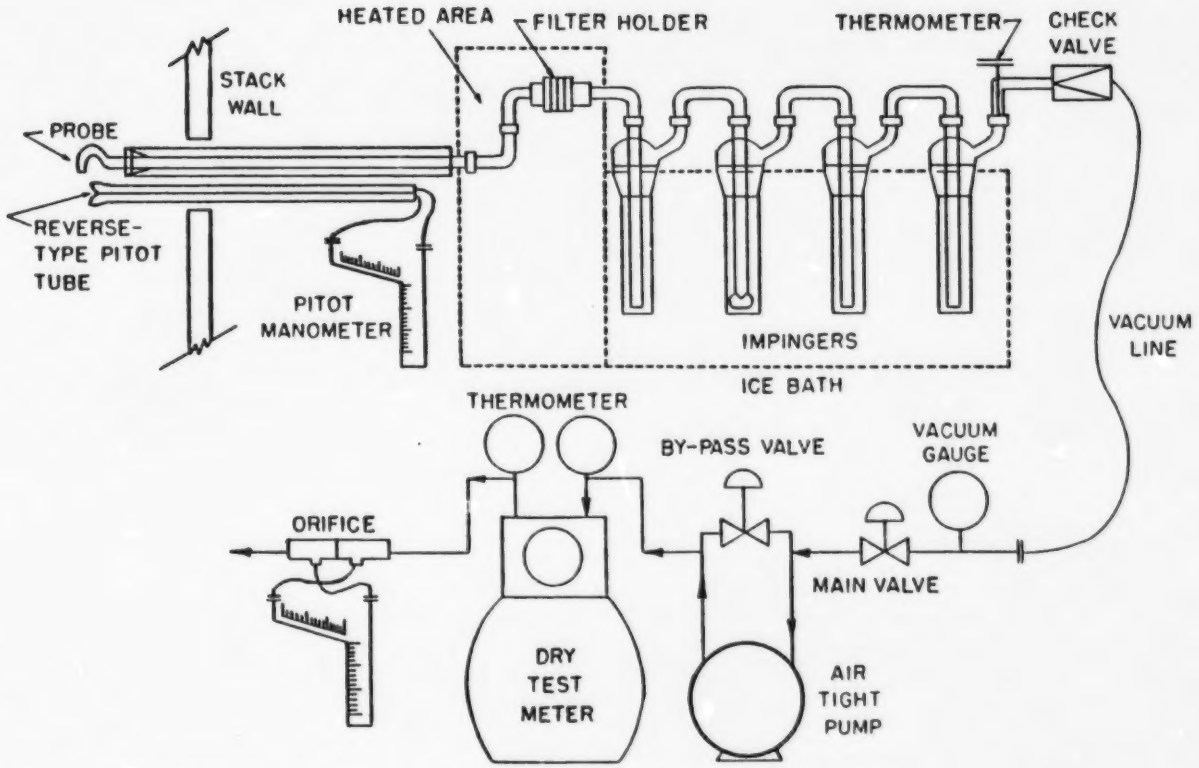

Figure 1. Particulate sampling train (EPA Method 5).

greater than 73 MW (250 million Btu/hr), the particulate emission allowed is 43 ng/J (0.10 lb/10^6 Btu) US EPA for units built after 1971. The standard reduces to 13 ng/J (0.03 lb/10^6 Btu) for units built after 1978 (Zieleniewski 1984).

2.2 Gaseous Sampling

The flue gases are also sampled for sulfur dioxide, nitrogen oxides and sulfuric acid, utilizing standard source test methods (Figures 2 to 4). A brief description of each test procedure follows.

The SO_2 gas in the stack is trapped by an aqueous 3% hydrogen peroxide solution and oxidized to $SO_4^=$ in the impingers. The dry gas meter totalizes the volume of air sampled, hence one can calculate the concentration of SO_2 in the gas stream. This can be expressed in grams per dry reference cubic metre or parts per million (ppm) or on the basis of the amount of coal burned per hour. The current EPA standard is 520 ng/J (1.2 lb SO_2 per million Btu) for large (>73 MW) coal fired boilers. One may combine the particulate test with an SO_2 test by substituting hydrogen peroxide in the impingers. The quantity of sulfate in the impingers can be determined using the barium-thorium titration procedure or by using ion chromatography. The latter technique is instrumental and is advantageous over the manual titration procedure.

Nitrogen oxides are sampled from the flue gas utilizing a grab sample approach. Three two litre flasks are evacuated to within three inches of total vacuum and the gas sample is extracted from the stack to each flask. The process only takes approximately 30 seconds per flask and one normally waits five minutes between samples. The solu-

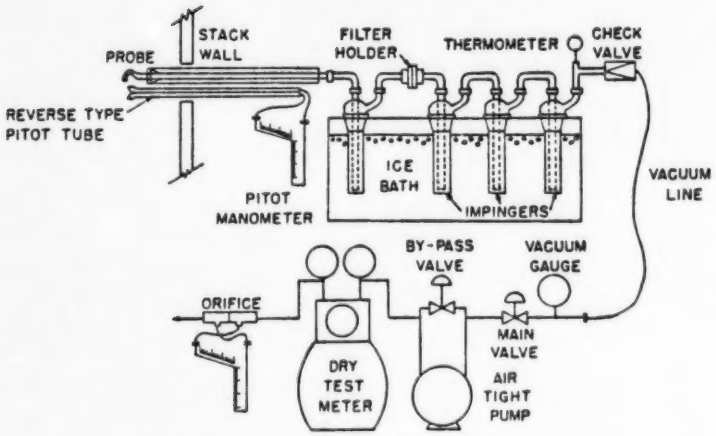

Figure 2. Sulfuric acid mist sampling train (EPA Method 8).

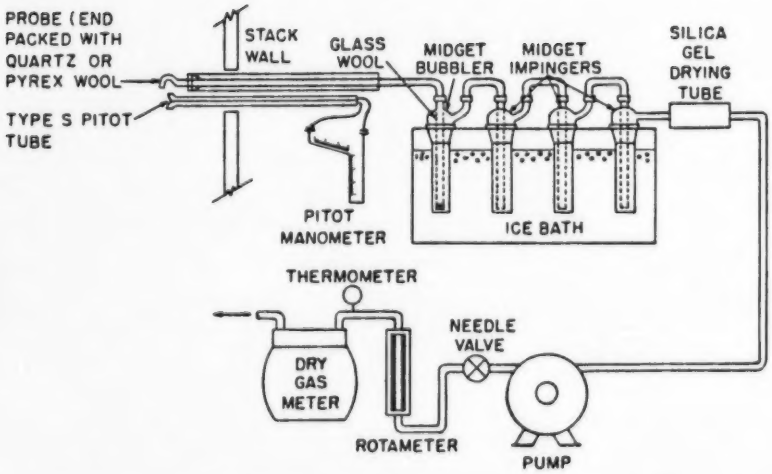

Figure 3. Sulfur dioxide sampling train (EPA Method 6).

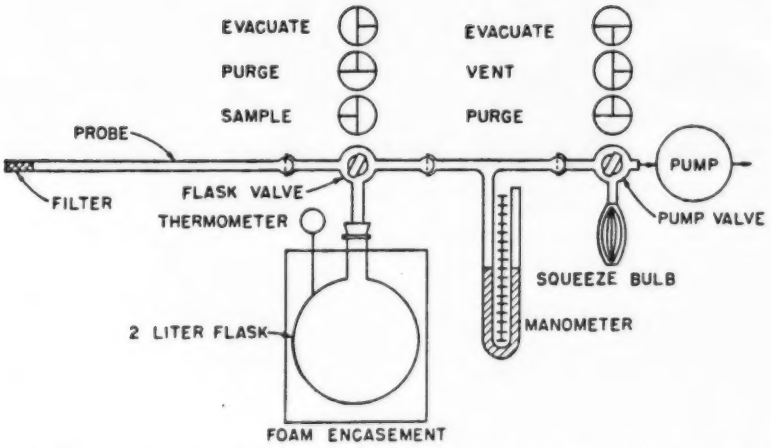

Figure 4. Nitrogen oxides sampling train (EPA Method 7).

tion used to trap the NO_x is a dilute solution of hydrogen peroxide and sulfuric acid. The NO and NO_2 is oxidized to $NO_3^=$ and neutralized with sodium hydroxide until analysis can be performed. Analysis can be done spectrophotometrically or by ion chromatograph.

EPA has come up with a new technique for NO_x determination using specially designed impingers. The solution used is 2% (W/W) sodium hydroxide and 4% potassium permanganate in water. This technique is an integrated approach to sampling and overcomes problems of grab sampling when the concentration of pollutants is not constant. The current standard for NO_x emission from large coal fired boilers is 260 ng/J (0.7 lb NO_x per million Btu) for lignite, bituminous, and anthracite coals.

Sulfuric acid mist is monitored using a heated glass probe maintained above the acid dew point of sulfuric acid which is approximately 130°C (266°F). A filter located between the first (80% isopropyl alcohol) and second impinger (3% hydrogen peroxide) prevents any carry-over of H_2SO_4 - alcohol solution. The contents of the first alcohol impinger and filter paper are analyzed for sulfate and represent the H_2SO_4 content. The next two impingers collect the sulfur dioxide fraction, hence one can separate sulfuric acid from sulfur dioxide.

2.3 In-stack Sizing

The size of particulate produced from a process stream is of vital interest to the environmental engineer. The design of air pollution control equipment must take into account the mass of particulate or gas and the particulate size.

Numerous instack inertial impactors are available commercially. These instruments utilize a multi-stage separation of mass based on inertial impaction. The sampler is fixed to the end of a stack sampling probe and fitted with the appropriate nozzle for isokinetic sampling (Figure 5). Stack gas is drawn through each stage which, in turn, represents a smaller area. The velocity is increased over each stage and particles of a certain size cannot follow the air stream and are impacted on a filter substrate (Figure 6). The weight on the filters is determined and graphed against the cutoff size for that stage. One may characterize the 50% point in the cumulative mass versus particle size as the mass median diameter (MMD). The MMD is usually in the 1-10 micron range for power utility boilers downstream of electrostatic precipitators.

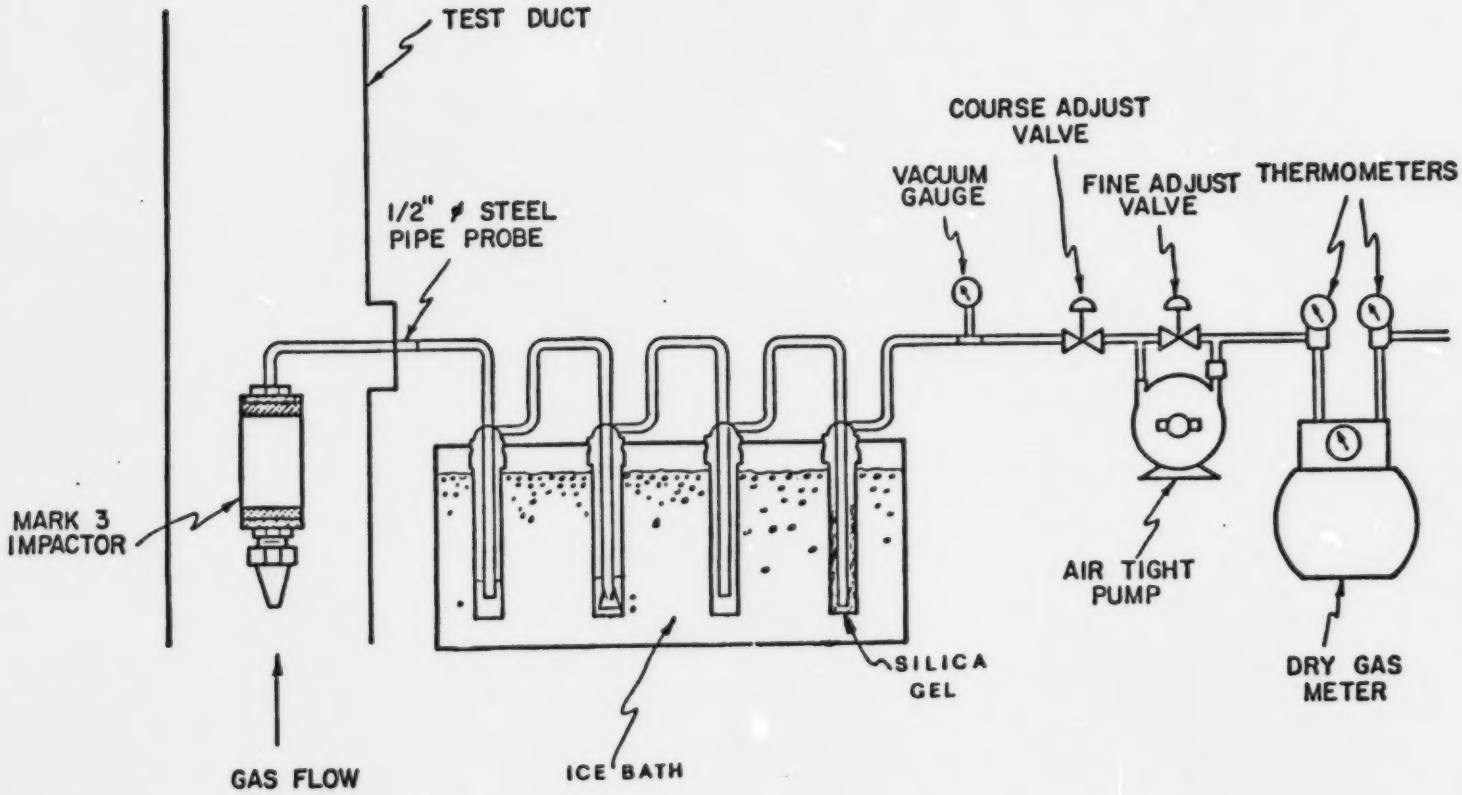

Fig. 5. UW MARK 3 CASCADE IMPACTOR SAMPLING TRAIN

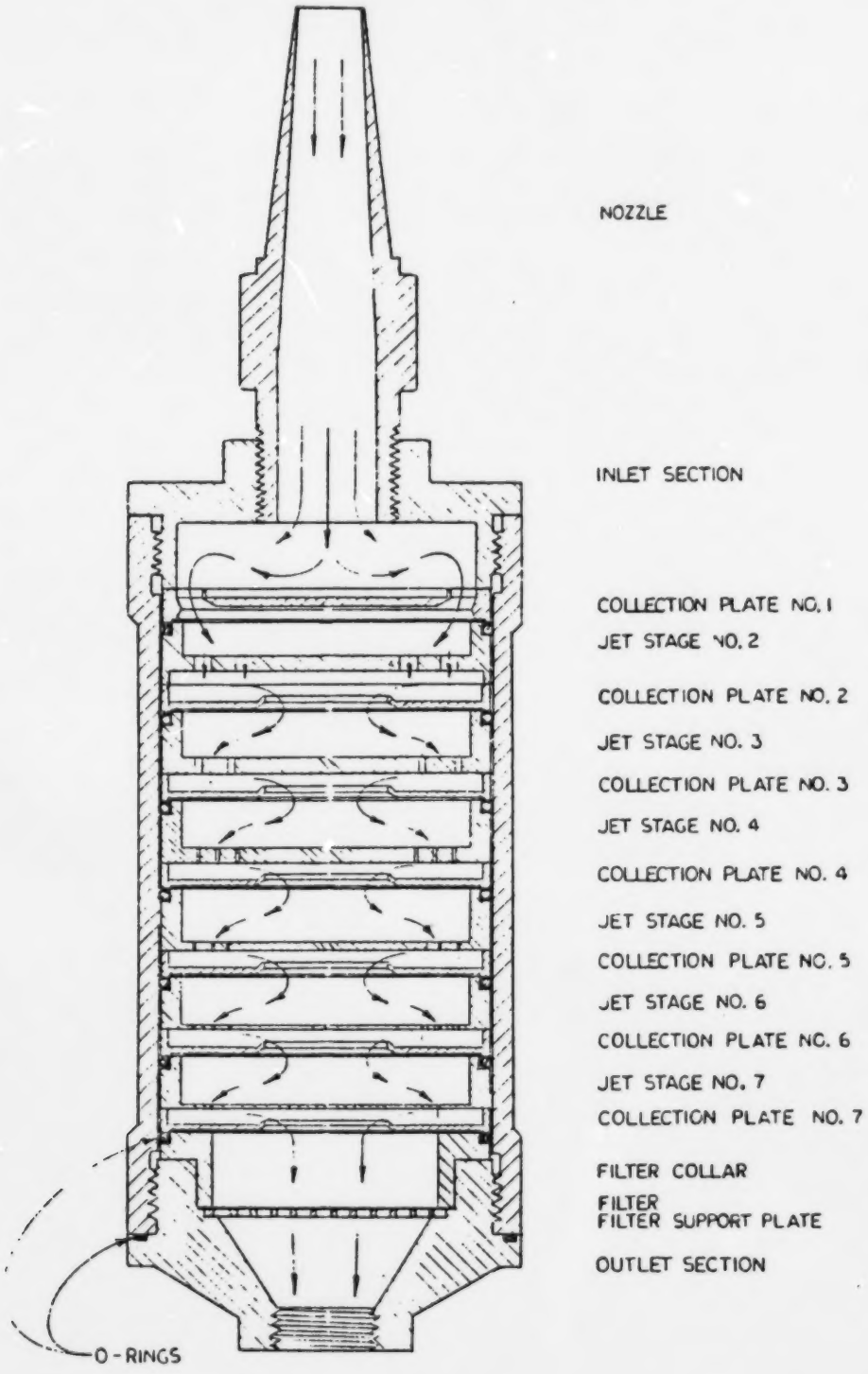

Fig. 6 Cross Section of Mark 3 Cascade Impactor

3 CONTINUOUS EMISSION MONITORS

In the fossil fuel fired steam generator industry, sulfur dioxide, nitrogen oxide content and opacity of the emission have to be monitored using continuous measuring equipment but there are exceptions in some cases. Opacity of the stream is determined by the concentration of the particulates in the stream. The continuous emission monitors (CEM) must be capable of monitoring emissions to ±20% accuracy with a confidence level of 95% (Brenchley 1982). In this way the regulatory bodies have a continuous measure of the concentrations of SO_2, NO_x and opacity.

Instruments are commercially available for measuring SO_2, NO_x, CO, HC (hydrocarbons), SO_3 and opacity. The most popular type of CEM utilizes the principle of nondispersive infrared analysis. A modulated infrared source of light is passed through two chambers, one is the reference cell and the other containing circulated stack gas. A detector monitors the difference in the two beams and because some infrared radiation is absorbed by SO_2 or other gaseous species this difference is indicative of the quantity of gaseous species.

Each chemical compound absorbs at discrete wavelengths, thus one can detect SO_2 in the presence of NO_2 or NO (Figure 7). Other types of CEM's rely on principles of ultraviolet (UV) spectroscopy, coulometric titration, conductivity, or colorimetry. CEM's have also been built to monitor stack aerosols (e.g. opacity). A light beam is focussed inside and near the top of the stack. The detector is mounted directly across from the light beam source on the opposite wall. As more aerosols (smoke) are emitted, the amount of detected light decreases in propor-

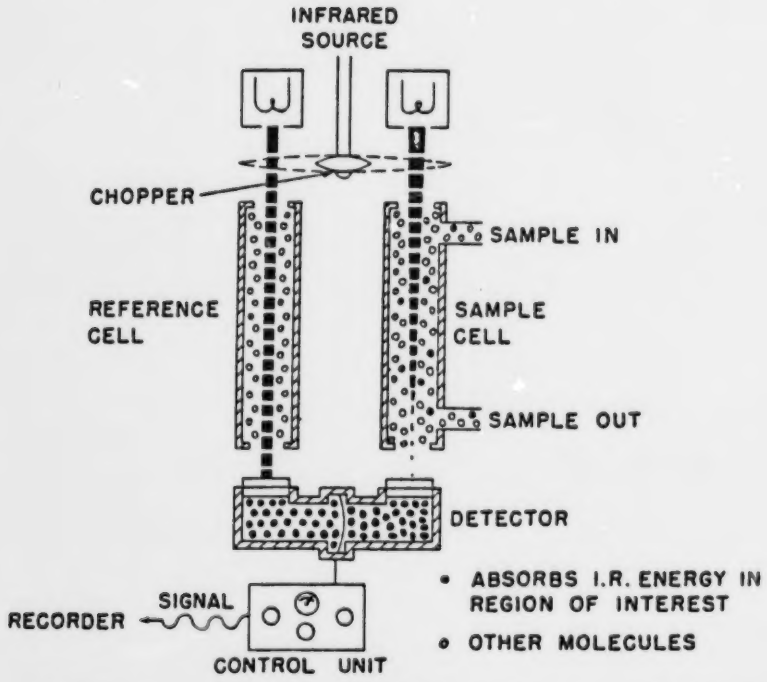

Figure 7 *Nondispersive infrared analyzer (courtesy of Beckman Instruments, Fullerton, California).*

tion to the quantity of smoke. Other instruments use a piezoelectric crystal vibrating at a known frequency in an electrical circuit. When more mass is added to the crystal, the frequency of oscillation decreases proportional to that mass.

The technique of beta absorption consists of the collection of a mass of particulates on a filter tape. The amount of beta radiation absorbed is proportional to the mass of particulates collected. The cost of the various CEM's can run from $5,000 to $30,000.

4 AMBIENT SAMPLING AND STANDARDS FOR PARTICULATES

The EPA National Ambient Air Quality Standard Branch (NAAQS) is proposing a regulation for particulate matter (PM) less than 10 microns aerodynamic diameter (PM_{10} standard). Health studies carried out over the last decade have shown a possible adverse health effect, particularly of the small particles (<10 microns) as they can penetrate into the lung (Van der Meulen 1986).

Instruments are available commercially that measure the fraction of particulate as coarse (2.5 to 10 microns) and fine (<2.5 microns). These instruments are called dichotomous samplers (Figure 8). The inlet to the dichotomous sampler directs the flow vertically upward. The air velocity is equal to the sedimentation velocity of a 10 micron particle. Larger particles (>10 microns) settle out and are not further separated. The smaller particles (<10 microns) are accelerated through the impactor nozzle and further separated by size. The coarse particles (2.5 to 10 microns) cannot follow the air streams and are deposited on a 37 mm filter paper at a flow rate of 0.1 cubic metre per hour. The fine particles (<2.5 microns) are collected on another 37 mm filter paper at 0.9 cubic metres per hour. A small fraction of the fine particulate (10%) is collected on the coarse filter, the fine particulate mass is adjusted for that fraction.

High volume air samplers operating at an aspiration rate of 68 cubic metres per hour with 10 micron inlets are commercially available. The increased flow provides a large sample of fine particulate matter for chemical or optical analysis. The new proposed PM_{10} standard will be based on high volume air sampling. The high volume samplers do not

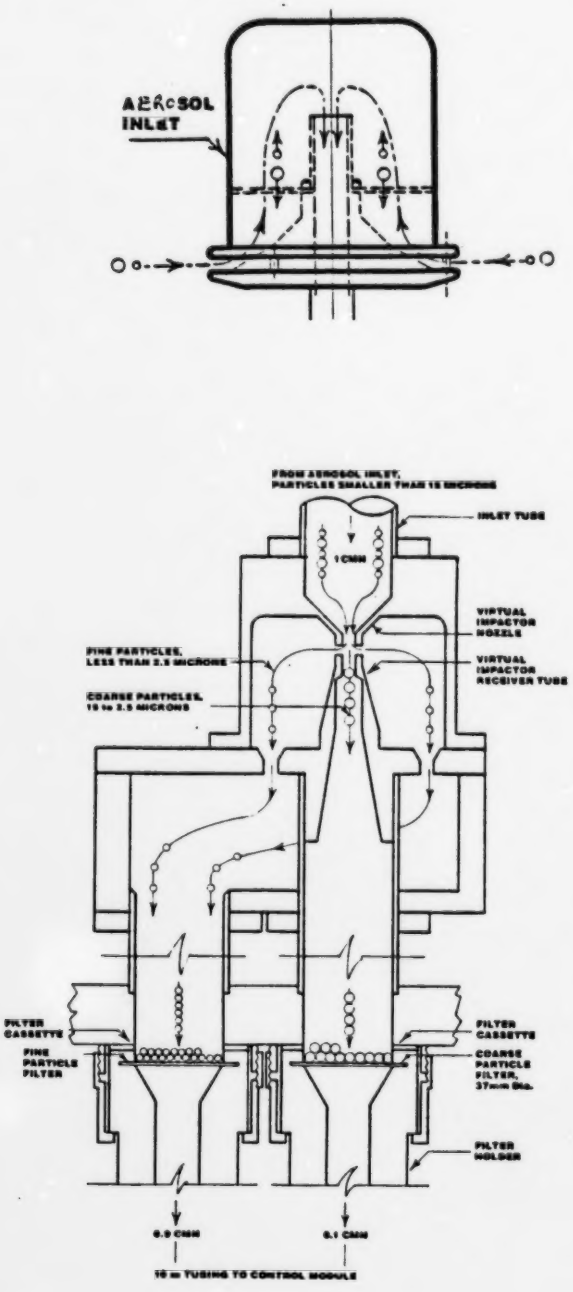

Figure 8. Dichotomous Sampler.

fractionate the suspended dust into two sizes. The size separation is accomplished in the same manner as the dichotomous sampler. The smaller particulates (<10 microns) are separated through a series of acceleration jets and colleciton plates. Particles smaller than 10 microns pass to the 20 x 25 cm high volume filter. The filter material can be glass fiber, cellulose or quartz fiber depending on proposed chemical analysis of the collected material.

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